

CRPAQS Filter Measurements Field Program

Final Report

Submitted to:

Karen Magliano

California Air Resources Board

By:

Steven D. Kohl

Desert Research Institute

January 26, 2005

Table of Contents

1. CRPAQS Field Study	1-1
2. Filter Measurements	2-1
2.1 Analysis Methods:	2-3
2.1.1 Gravimetric Analysis	2-3
2.1.2 Elements by XRF	2-3
2.1.3 Elemental and Organic Carbon	2-3
2.1.4 Inorganic Ion Analyses	2-5
2.1.5 Ion Chromatographic Analysis for Chloride, Nitrate, and Sulfate	2-5
2.1.6 Ammonium Analysis	2-6
2.1.7 Atomic Absorption Analysis for Soluble metals	2-7
2.2 Measurement Validity	2-9
3. Database Structures and Features	3-1
4. References	4-4

1. CRPAQS FIELD STUDY

The CRPAQS aerosol monitoring network is shown in Figure 1.1-1. Measurements of precursor gases and PM taken during CRPAQS included: 1) gaseous NH_3 and HNO_3 by the denuder difference method with DRI medium-volume sequential gas samplers (SGS) at the anchor sites; 2) $\text{PM}_{2.5}$ and NH_3 by DRI sequential filter samplers (SFS) equipped with Bendix 240 cyclone inlets and preceding nitric acid denuders at the anchor sites; and 3) $\text{PM}_{2.5}$, PM_{10} , and NH_3 by battery-powered Airmetrics Minivol samplers at the satellite sites. $\text{PM}_{2.5}$ and PM_{10} mass, filter transmission (b_{abs}), 40 elements (Na to U; Watson et al., 1999), ions (Cl^- , NO_3^- , SO_4^{2-} , Na^+ , K^+ , NH_4^+ ; Chow and Watson, 1999), volatilized NO_3^- , and seven-fraction organic and elemental carbon were acquired.

Measurements of gaseous and particulate organic compounds included: 1) 123 volatile organic compounds (VOCs) from C_2 to C_{12} by canister sampling and gas chromatography/mass spectrometry (GC/MS) analysis, 2) 63 VOCs from C_8 to C_{20} by Tenax-TA cartridge sampling with analysis by the thermal desorption/cryogenic preconcentration method followed by high-resolution gas chromatography separation and flame ionization detection and/or combined mass spectrometry/Fourier transform infrared detection, 3) 14 carbonyl compounds by dinitrophenylhydrazine (DNPH) cartridge sampling and high-performance liquid chromatography analysis, and 4) 151 semivolatile organic compounds (SVOCs) and particulate organics sampled with DRI organic sampling systems at 4 anchor sites (Angiola, Bethel Island, Fresno, and Sierra Foothill) and with Minivol samplers equipped with Teflon-impregnated glass-fiber filters at the 20 satellite sites and analyzed by gas chromatography/mass spectrometry. Table 1.1-1 summarizes measurements acquired from the CRPAQS network.

The annual anchor network includes 14 months of daily $\text{PM}_{2.5}$ sampling between 12/03/99 and 02/03/01 at two major urban centers (Fresno [FSF] and Bakersfield [BAC]) to represent community human exposure, and at one intrabasin gradient and vertical gradient site (Angiola [ANGI]) located in a flat field ~85 km south/southeast of Fresno to represent environments with minimal influences from urban or non-urban sources. Two additional anchor sites (Bethel Island [BTI] and Sierra Foothill [SNFH]) were added during the 15-day, 5 times/day winter intensive program for both $\text{PM}_{2.5}$ and gaseous NH_3 and HNO_3 measurements. Measurements of VOCs (C_2 to C_{20}) and carbonyls were taken 4 times/day during the winter intensive program at 4 anchor sites (Angiola, Bethel Island, Fresno, and Sierra Foothill). To achieve adequate loadings for heavy hydrocarbons, SVOCs and particulate organics were sampled 2 times/day at the Angiola, Bethel Island, and Sierra Foothill anchor sites and 4 times/day at the Fresno anchor site during the winter intensive.

The satellite network included annual, fall intensive, and winter intensive sampling programs at a total of 53 sites in 8 categories defined by environmental characteristics surrounding the sites (as noted in Table 1.1-1) and included 18 community exposure sites, 11 emissions source dominated sites, 9 visibility sites, 11 intrabasin gradient sites, 2 vertical

Figure 1.1-1. Map of monitoring sites in the CRPAQS network (the fall intensive study's 11 PM₁₀ sites are not shown).

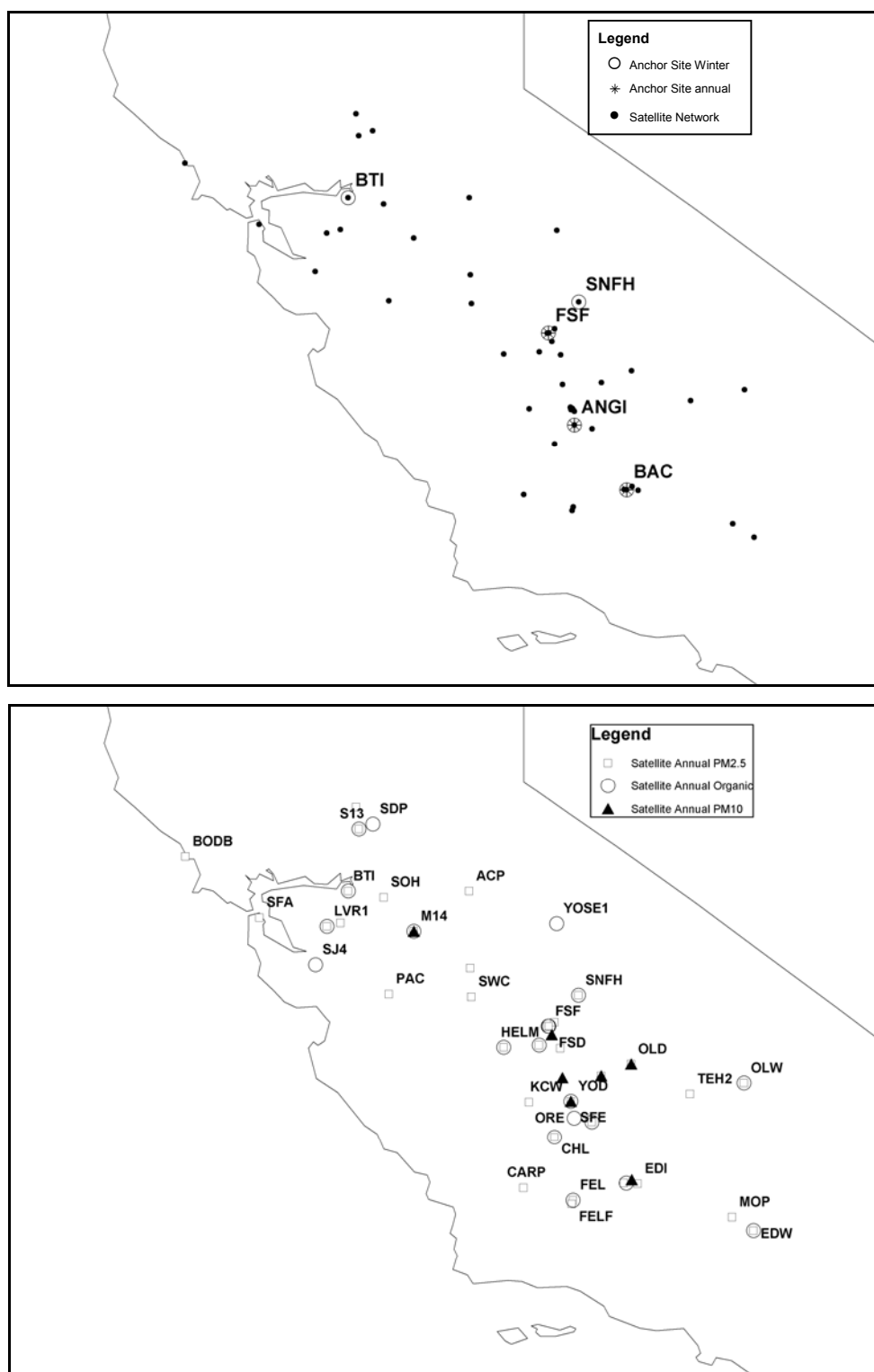


Table 1.1-1. Summary of CRPAQS anchor and satellite site aerosol measurements.^a

Site Code	Site Name	Site Type	ANCHOR SITES		SATELLITE SITES ^b							
			Sampling Period		Filter Pack					Sampling Period		
			Annual ^c	Winter Intensive ^d	PM _{2.5}		PM _{2.5} Organics	PM ₁₀		Annual ^e	Fall Intensive ^f	Winter Intensive ^g
					T/C	q/n	TIGF	T/c	Q/n			
		<i>Minivol module →</i>			<i>A^h</i>	<i>Bⁱ</i>	<i>D^j</i>	<i>g^k</i>	<i>h^l</i>			
ACP	Angels Camp	Intrabasin Gradient			FTC	FQN				X		X
ALT1	Altamont Pass ^m	Interbasin Transport			FTC					X		X
ANGI	Angiola-ground level	Intrabasin Gradient, Vertical Gradient, Visibility	X	X			TIGF			X		
BAC	Bakersfield-5558 California Street	Community Exposure, Visibility	X	X			TIGF			X		
BGS	Bakersfield-1120 Golden State	Community Exposure						TTC	TQN	(X)		
BODG	Bodega Marine Lab	Boundary/Background			FTC	FQN				X		X
BRES	BAC-Residential	Source- woodburning			FTC	FQN				X		X
BTI	Bethel Island	Interbasin Transport		X	FTC	FQN	TIGF			X		
CARP	Carrizo Plain ^m	Intrabasin Gradient, Visibility			FTC					X		
CHL	China Lake	Visibility			FTC	FQN	TIGF			X		
CLO	Clovis	Community Exposure			FTC	FQN				X		X
CO5	Corcoran Railroad Shoulder	Source - Railroad/ Unpaved Shoulder						TTC			X	
COP	Corcoran-Patterson Avenue	Community Exposure			FTC	FQN	TIGF	TTC	TQN	(X)	X	X
DAIP	Dairy Road - Paved	Source - Paved Road						TTC			X	
DAIU	Dairy Road - Unpaved	Source-Unpaved Road						TTC			X	
EDI	Edison ^m	Intrabasin Gradient			FTC					X		X
EDW	Edwards Air Force Base	Intrabasin Gradient, Visibility			FTC	FQN	TIGF			X		
FEDL	Feedlot or Dairy	Source - Cattle			FTC	FQN	TIGF			X		X
FEL	Fellows	Source- Oilfields			FTC	FQN	TIGF			X		X
FELF	Foothills above Fellows	Intrabasin Gradient			FTC	FQN				X		X
FREM	Fresno MV	Source - Motor Vehicle			FTC	FQN				X		X
FRES	Residential area near FSF, with woodburning	Source - Woodburning			FTC	FQN	TIGF			X		X
FSD	Fresno Drummond	Community Exposure						TTC	TQN	(X)		
FSF	Fresno-3425 First Street	Community Exposure, Visibility	X	X			TIGF			X		
GRA	Grain Elevator	Source - Grain Elevators						TTC	TQN		X	
GRAS	Grain Elevator South	Source - Zone of Influence						TTC	TQN		X	
H43	Highway 43	Southern Boundary						TTC	TQN		X	
HAN	Hanford-Irwin St.	Community Exposure and Fall Northern Boundary						TTC	TQN	(X)	X	
HELM	Agricultural fields/Helm-Central Fresno County	Intrabasin Gradient			FTC	FQN	TIGF			X		X
KCW	Kettleman City ^m	Intrabasin Gradient			FTC					X		X
LVR1	Livermore - New site	Interbasin Transport			FTC	FQN	TIGF			X		X

Site Code	Site Name	Site Type	ANCHOR SITES		SATELLITE SITES ^b							
			Sampling Period		Filter Pack					Sampling Period		
			Annual ^c	Winter Intensive ^d	PM _{2.5}		PM _{2.5} Organics	PM ₁₀		Annual ^e	Fall Intensive ^f	Winter Intensive ^g
					T/C	q/h	TIGF	T/c	Q/h			
		<i>Minivol module →</i>			<i>A^h</i>	<i>Bⁱ</i>	<i>D^j</i>	<i>g^k</i>	<i>h^l</i>			
M14	Modesto 14th St.	Community Exposure			FTC	FQN	TIGF	TTC	TQN	(X)		X
MOP	Mojave-Poole	Community Exposure			FTC	FQN				X		
MRM	Merced-midtown	Community Exposure			FTC	FQN				X		X
OLD	Oildale-Manor	Community Exposure			FTC	FQN		TTC	TQN	(X)		
OLW	Olancho	Background			FTC	FQN	TIGF			X		X
ORE	Oregon Avenue	Fall Neighborhood Exposure						TTC			X	
PAC1	Pacheco Pass ^m	Interbasin Transport			FTC					X		
PIXL	Pixley Wildlife Refuge	Rural, Intrabasin Gradient			FTC	FQN	TIGF			X		X
PLE	Pleasant Grove (north of Sacramento)	Intrabasin Gradient			FTC	FQN				X		
S13	Sacramento-1309 T Street	Community Exposure			FTC	FQN	TIGF			X		X
SDP	Sacramento-Del Paso Manor	Community Exposure					TIGF			X		
SELM	Selma(south Fresno area gradient site)	Community Exposure			FTC	FQN				X		X
SFA	San Francisco - Arkansas	Community Exposure			FTC	FQN				X		
SFE	Santa Fe Street	Source - Cotton Handling						TTC	TQN		X	
SJ4	San Jose-4th Street	Community Exposure					TIGF			X		
SNFH	Sierra Nevada Foothills	Vertical Gradient, Intrabasin Gradient, Visibility		X	FTC	FQN	TIGF			X		
SOH	Stockton-Hazelton	Intrabasin Gradient			FTC	FQN				X		X
SWC	SW Chowchilla	Interbasin Transport			FTC	FQN				X		X
TEH2	Tehachapi Pass ^m	Interbasin Transport, Visibility			FTC					X		X
VCS	Visalia Church St.	Community Exposure			FTC	FQN		TTC	TQN	(X)		X
YOD	Yoder Street	Fall Northern Edge of Source Area						TTC			X	
YOSE1	Yosemite National Park-Turtleback Dome	Boundary/Background, Visibility					TIGF			X		
			-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
		Total Number of Sites	3	5	35	29	20	16	11	44	11	25
		18	community exposure sites (SDP, S13, SJ4, SFA, MRM, M14, CLO, FSF, SELM, VCS, HAN, COP, FSD, BGS, OLD, BAC, MOP, and ORE)									
		11	emissions source dominated sites (FRES, FREM, FEDL, GRA, GRAS, SFE, BRES, FEL, CO5, DAIP, and DAIU)									
		9	visibility sites (YOSE1, SNFH, FSF, ANGI, CHL, BAC, CARP, TEH2, and EDW)									
		11	intrabasin gradient sites (PLE, ACP, SOH, SNFH, HELM, KCW, ANGI, PIXL, EDI, FELF, and EDW)									
		2	vertical gradient sites (SNFH and ANGI)									
		1	intrabasin transport site (ACP)									
		6	interbasin transport sites (BTI, ALT1, LVR1, PAC1, SWC, and TEH2)									
		7	boundary/background sites (BODG, YOSE1, HAN, OLW, H43, PIXL, and YOD)									

(X) Includes the seven PM₁₀ sites operated during the annual program.

- ^a Teflon-membrane filter samples were analyzed for mass by gravimetry, filter transmission (b_{abs}) by densitometry, and elements (Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Se, Br, Rb, Sr, Y, Zr, Mo, Pd, Ag, Cd, In, Sn, Sb, Ba, La, Au, Hg, Tl, Pb, and U) by x-ray fluorescence (Watson et al., 1999); quartz-fiber filter samples were analyzed for anions (Cl⁻, NO₃⁻, SO₄⁻) by ion chromatography (Chow and Watson, 1999), ammonium by automated colorimetry, water-soluble Na⁺ and K⁺ by atomic absorption spectrophotometry, and 7-fraction organic and elemental carbon (OC1 combusted at 120 °C, OC2 at 250 °C, OC3 at 450 °C, OC4 at 550 °C, EC1 at 550 °C, EC2 at 700 °C, and EC3 at 800 °C with pyrolysis correction) by thermal/optical reflectance (Chow et al., 1993a, 2001); citric-acid-impregnated filter samples were analyzed for ammonia by automated colorimetry; and sodium-chloride-impregnated filters were analyzed for volatilized nitrate by ion chromatography.
- ^b Sampling with battery-powered Minivol samplers (Airmetrics, Eugene, OR) equipped with PM₁₀/PM_{2.5} (in tandem) or PM₁₀ inlets at a flow rate of 5 L/min.
- ^c Anchor site annual sampling program used DRI medium-volume sequential filter samplers (SFS) equipped with Bendix 240 cyclone PM_{2.5} inlets and preceding anodized aluminum nitric acid denuders. Sampling was conducted daily, 24 hours/day (midnight to midnight) from 12/02/99 to 02/03/01 at a flow rate of 20 L/min. Two filter packs were used for sampling: 1) each Teflon/citric acid filter pack consists of a front Teflon-membrane filter (for mass, b_{abs}, and elemental analyses) backed up by a citric-acid-impregnated cellulose-fiber filter (for ammonia), and 2) each quartz/NaCl filter pack consists of a front quartz-fiber filter (for ion and carbon analyses) backed up by a sodium-chloride-impregnated cellulose-fiber filter (for volatilized nitrate).
- ^d Anchor site winter intensive sampling included both SFS for PM_{2.5} sampling and sequential gas samplers (SGS) for ammonia and nitric acid sampling by denuder difference on 15 forecast episode days (12/15/00 to 12/18/00, 12/26/00 to 12/28/00, 01/04/01 to 01/07/01, and 01/31/01 to 02/03/01). The two SGS were equipped with: 1) citric-acid-coated glass denuders and quartz-fiber filters backed up by citric-acid-impregnated cellulose-fiber filters for ammonia (NH₃); and 2) anodized aluminum denuders and quartz-fiber filters backed up by sodium-chloride-impregnated cellulose-fiber filters for nitric acid (HNO₃). VOCs and carbonyls were sampled 4 times/day (0000-0500, 0500-1000, 1000-1600, and 1600-2400) at 4 anchor sites (Angiola, Fresno, Bethel Island, and Sierra Foothill). Heavy hydrocarbons were sampled with Tenax and PUF/XAD samplers 4 times/day (0000-0500, 0500-1000, 1000-1600, and 1600-2400) at the Fresno anchor site and 2 times/day (0500-1600 and 1600-next day 0500) at the Bethel Island, Sierra Foothill, and Angiola anchor sites.

C₂ to C₁₂ volatile organic compound (VOC) samples were acquired with canister samplers and analyzed by Dr. Reinhold Rasmussen at the Oregon Graduate Institute of Science and Technology, Portland, OR, using gas chromatography with mass spectrometry to determine concentrations of 123 VOCs:

propene	4-methyl-1-pentene	1-methylcyclopentene	2,3-dimethylhexane	n-nonane	indene
propane	3-methyl-1-pentene	benzene	2-methylheptane	isopropylbenzene	1,3-diethylbenzene
isobutane	cyclopentane	3,3-dimethylpentane	4-methylheptane	isopropylcyclohexane	1,4-diethylbenzene
1,3-butadiene	2,3-dimethylbutane	cyclohexane	3-methylheptane	2,6-dimethyloctane	n-butylbenzene
n-butane	methyl-t-butylether	4-methylhexene	2,2,5-trimethylhexane	alpha-pinene	1,2-diethylbenzene
methanol	2-methylpentane	2-methylhexane	octene-1	3,6-dimethyloctane	1,3-dimethyl-4-ethylbenzene
t-2-butene	2,2-dimethylpentane	2,3-dimethylpentane	1,1-dimethylcyclohexane	n-propylbenzene	isopropyltoluene
1&2-butyne	3-methylpentane	cyclohexene	n-octane	m-ethyltoluene	nonanal
c-2-butene	2-methyl-1-pentene	3-methylhexane	2,3,5-trimethylhexane	p-ethyltoluene	1-undecene
3-methyl-1-butene	1-hexene	1,3-dimethylcyclopentane	2,4-dimethylheptane	1,3,5-trimethylbenzene	n-undecane
ethanol	n-hexane	3-ethylpentane	4,4-dimethylheptane	o-ethyltoluene	1,2,4,5-tetramethylbenzene
isopentane	t-3-hexene	1-heptene	2,6-dimethylheptane	octanal	1,2,3,5-tetramethylbenzene
1-pentene	t-2-hexene	2,2,4-trimethylpentane	2,5-dimethylheptane	beta-pinene	1,2,3,4-tetramethylbenzene
2-methyl-1-butene	2-methyl-2-pentene	t-3-heptene	3,3-dimethylheptane	1-decene	2-methylindan
n-pentane	cis-3-methyl-2-pentene	n-heptane	ethylbenzene	1,2,4-trimethylbenzene	1-methylindan
isoprene	c-3-hexene	2,4,4-trimethyl-1-pentene	m- & p-xylene	n-decane	1-dodecene
t-2-pentene	c-2-hexene	methylcyclohexane	2-methyloctane	isobutylbenzene	naphthalene
c-2-pentene	trans-3-methyl-2-pentene	2,5-dimethylhexane	3-methyloctane	sec-butylbenzene	n-dodecane
2-methyl-2-butene	methylcyclopentane	2,4-dimethylhexane	styrene	1,2,3-trimethylbenzene	
2,2-dimethylbutane	2,4-dimethylpentane	2,3,4-trimethylpentane	o-xylene	limonene	
cyclopentene	2,2,3-trimethylbutane	toluene	1-nonene	indan	

C₈ to C₂₀ volatile organic compound samples were acquired with glass cartridges filled with Tenax-TA (a polymer of 2,6-diphenyl-p-phenylene oxide) solid adsorbent and analyzed by the thermal desorption/cryogenic preconcentration method followed by high-resolution gas chromatography separation and flame ionization detection and/or combined mass spectrometry/Fourier transform infrared detection for 63 VOCs:

1,2,4,5-tetramethylbenzene	(1-methylethyl)benzene	1,4-diethylbenzene	1,3-diethylbenzene	1,2,3,4-tetramethylbenzene
1(1,1-dimethylethyl)3-5-dimethylbenzene	1-methyl-4-(1-methylethyl)benzene	1,2-diethylbenzene	(1-methylpropyl)benzene	2,3-dihydroindene (indan)

1,2,3,5-tetramethylbenzene	1,3-dimethyl-4-ethylbenzene	1,3-di-n-propylbenzene	Tetradecanal
1-methyl-2-(1-methylethyl)benzene	1,2-dimethyl-3-ethylbenzene	2-methylnaphthalene	Pentadecanal
1-methyl-3-(1-methylethyl)benzene	1,3-dimethyl-5-ethylbenzene	1-methylnaphthalene	Hexadecanal
n-pentylbenzene	1,2-dimethyl-4-ethylbenzene	hexanal	Octadecanal
(2-methylpropyl)benzene	1-methyl-2-n-propylbenzene	heptanal	2-furaldehyde
1-methyl-2-ethylbenzene	1-methyl-3-n-propylbenzene	octanal	benzaldehyde
1-methyl-3-ethylbenzene	1-methyl-4-n-propylbenzene	nonanal	acetophenone
1-methyl-4-ethylbenzene	1-methyl-2-n-butylbenzene	decanal	2,5-dimethylbenzaldehyde
4-methylindan	1,4-dimethyl-2-ethylbenzene	undecanal	ethanone-1(3-methoxyphenol)
2-methylindan	1,3-dimethyl-2-ethylbenzene	dodecanal	t-2,4-decadienal
5-methylindan	1-ethyl-2-n-propylbenzene	tridecanal	Undecane

dodecane
tridecane
tetradecane
pentadecane
hexadecane
heptadecane
octadecane
nonadecane
eicosane

Carbonyl samples were acquired with AtmAA sequential carbonyl samplers and analyzed by Dr. Kochy Fung at AtmAA Environmental Consultants, Calabasas, CA, using high-performance liquid chromatography to determine concentrations of 14 carbonyls (formaldehyde, acetaldehyde, acetone, acrolein, propanal, crotonal, methyl ethyl ketone, methacrolein, butanal, pentanal, glyoxal, hexanal, benzaldehyde, and m-tolualdehyde). Particulate and semivolatile organic compound samples were acquired with DRI Organic Sampling System samplers on Teflon-impregnated glass fiber filters backed up with a PUF/XAD-4/PUF sandwich solid adsorbents and analyzed by gas chromatography with mass spectrometry for 151 particulate and semivolatile VOCs:

Naphthalene	Benz(a)anthracene	9-anthraldehyde	Carpanes	n-pentacosane
2-menaphthalene	7-methylbenz[a]anthracene	Benzanthrone	8, 13-Dimethyl-14-n-butylpodocarpane	n-hexacosane
1-menaphthalene	Chrysene/triphenylene	Benz(a)anthracene-7,12-dione	8, 13Dimethyl-14-[3'-methylbutyl] podocarpane	n-heptacosane
2,6+2,7-dimenaphthalene	Benzo(b+j+k)FL	1,4-chrysenequinone	n-Alkanoic Acids	n-octacosane
1,7+1,3+1,6-dimenaphthalene	BeP	9,10-dihydrobenzo(a)pyren-7(8H)-one	octanoic acid	farnesane
2,3+1,4+1,5-dimenaphthalene	BaP	Nitro-PAH	nonanoic acid	norpristane
1,2-dimenaphthalene	7-methylbenzo[a]pyrene	1-Nitronaphthalene	decanoic acid	norfarnesane
1,8-dimenaphthalene	indeno[123-cd]pyrene	2-Nitronaphthalene	undecanoic acid	pristane
Biphenyl	dibenz(ah+ac)anthracene	Methylnitronaphthalenes	dodecanoic acid	phytane
2-methylbiphenyl	Benzo(b)chrysene	2-Nitrobiphenyl	tridecanoic acid	
3-methylbiphenyl	Benzo(ghi)perylene	4-Nitrobiphenyl	tetradecanoic acid	<u>Saturated Cycloalkanes</u>
4-methylbiphenyl	coronene	5-Nitroacenaphthene	heptadecanoic acid	tridecylcyclohexane
Trimethylnaphthalene Isomers	4Hcyclopenta(def)phenanthrene	2-Nitrofluorene	octadecanoic acid	tetradecylcyclohexane
Ethyl-Methylnaphthalenes	benzo(c)phenanthrene	9-Nitroanthracene	nonadecanoic acid	pentadecylcyclohexane
Acenaphthylene	Perylene	1-Nitropyrene	eicosanoic acid	hexadecylcyclohexane
Acenaphthene	quinoline	4-Nitropyrene	Alkanedioic acids	heptadecylcyclohexane
phenanthrene	dibenzo[a,e]pyrene	3-Nitrofluoranthene	octadecanedioic acid	octadecylcyclohexane
Fluorene	dibenzo[a,h]pyrene	7-Nitrobenz(a)anthracene	nonadecanedioic acid	nonadecylcyclohexane
Methylfluorenes Isomers	dibenzo[a,i]pyrene	6-Nitrochrysene	Aromatic acids	
1-methylfluorene	dibenzo[a,l]pyrene	6-Nitrobenzo(a)pyrene	benzoic acid	<u>Lower priority cycloalkanes</u>
Methylphenanthrenes Isomers	dibenz[a,j]acridine	1,8-Dinitropyrene	methylbenzoic acid	heptylcyclohexane
2-methylphenanthrene	dibenz[a,h]acridine	1,6-Dinitropyrene		octylcyclohexane
1-methylphenanthrene	7H-dibenzo[c,g]carbazole	1,3-Dinitropyrene		nonylcyclohexane
3,6-dimethylphenanthrene	5-methylchrysene			decylcyclohexane
1,7-dimethylphenanthrene	dibenz[a,h]anthracene	<u>Hopanes&Steranes</u>		undecylcyclohexane
Anthracene	7,12-dimethylbenzanthracene	18(H)-22,29,30-trisnorheohopane		dodecylcyclohexane
9-methylanthracene	3-methylcholanthrene	17(H)-22,29,30-trisnorhopane		eicosylcyclohexane
fluoranthene	Oxy-PAH	17(H)-21(H)-29-norhopane		heneicosycyclohexane
pyrene	9-fluorenone	17(H)-21(H)-hopane		
Methylpyrene/fluoranthenes	Xanthone	20R,5(H),14 (H),17(H)-cholestane		
4-methylpyrene	Acenaphthenequinone	20R,5(H),14(H),17(H)-cholestane		
retene	Perinaphthenone	20R&S,5(H),14(H),17(H)-ergostane		
Benzonaphthothiophene	Anthraquinone	20R&S,5(H),14(H),17(H)-sitostane		

- ^e Satellite site annual sampling program included every-sixth-day 24-hour sampling at 35 PM_{2.5} sites and 7 PM₁₀ sites between 12/02/99 and 02/03/01. Particulate organic compounds were sampled at 20 sites between 02/06/00 and 01/31/01.
- ^f Satellite site fall intensive study included 24-hour sampling of PM₁₀ on 37 days between 10/09/00 and 11/14/00 at 11 sites. 6 sites (COP, H43, HAN, GRA, GRAS, and SFE) were equipped with both Teflon/citric acid and quartz/NaCl filter packs. 5 sites (CO5, DAIP, DAIU, ORE, and YOD) were equipped with only Teflon/citric acid filter packs.
- ^g Satellite site winter intensive study included 24-hour sampling of PM_{2.5} on 13 forecast episode days (12/15/00 to 12/18/00, 12/25/00, 12/27/00, 12/28/00, 01/04/01 to 01/06/01, and 02/01/01 to 02/03/01) at 25 PM_{2.5} sites, with 21 of the sites equipped with both Teflon/citric acid and quartz/NaCl filter packs.
- ^h Minivol module A: PM_{2.5} Teflon/citric acid filter packs at 35 satellite sites. Each filter pack consisted of a front Teflon-membrane filter (for mass, b_{abs}, and elements) backed up by a citric-acid-impregnated cellulose-fiber filter (for ammonia).
- ⁱ Minivol module B: PM_{2.5} quartz/NaCl filter packs at 29 satellite sites (same sites as module A but excluding ALT1, PAC1, KCW, EDI, CARP, and TEH2). Each filter pack consisted of a front pre-fired quartz-fiber filter (for ions and carbon) backed up by a sodium-chloride-impregnated cellulose-fiber filter (for volatilized nitrate).
- ^j Minivol module D: PM_{2.5} Teflon-impregnated glass-fiber filters (TIGF) at a total of 20 sites (including 3 annual anchor sites [Fresno, Angiola, and Bakersfield], 14 annual satellite sites, the San Jose-4th St. [SJ4] site, the Sacramento-Del Paso Manor [SPP] site, and the Yosemite [YOSE1] site). A total of 61 samples acquired over the yearlong sampling period were composited as one sample and analyzed by gas chromatography with mass spectrometry (GC/MS) for 151 particulate organic compounds as listed in footnote d above.
- ^k Minivol module g: PM₁₀ Teflon/citric acid filter packs at 16 satellite sites, 4 of which (M14, VCS, COP, and OLD) were collocated with annual PM_{2.5} measurements, and 7 of which (M14, VCS, COP, FSD, BGS, HAN, and OLD) were annual PM₁₀ sites. Each filter pack consisted of a front Teflon-membrane filter (for mass, b_{abs}, and elements) backed up by a citric-acid-impregnated cellulose-fiber filter (for ammonia).
- ^l Minivol module h: PM₁₀ quartz/NaCl filter packs at 16 satellite sites, 4 of which were collocated with annual PM_{2.5} measurements (M14, VCS, COP, and OLD), and 7 of which (M14, VCS, COP, FSD, BGS, HAN, and OLD) were annual PM₁₀ sites. Each filter pack consisted of a front quartz-fiber filter (for ion and carbon analyses) backed up by a sodium-chloride-impregnated cellulose-fiber filter (for volatilized nitrate).
- ^m One of six sites (ALT1, PAC1, KCW, EDI, CARP, and TEH2) where only Minivol module A Teflon/citric acid filter packs were acquired.

gradient sites, 1 intrabasin transport site, 6 interbasin transport sites, and 7 boundary/background sites. The satellite sites were designed to: 1) examine spatial variations of PM concentrations within the study domain, 2) identify potential pollutant transport in the prevailing wind direction, 3) determine the zones of influence of specific emitters (e.g., fugitive dust) on PM loadings in a mixed-land-use area, and 4) evaluate the zones of representation of single-site measurements for community exposure to PM. The satellite sites within the air basin represent middle-scale (0.1 to 0.5 km), neighborhood-scale (0.5 to 4 km), and urban-scale (4 to 100 km) influences around the anchor sites, whereas the inter- or intrabasin gradient sites and boundary/background sites represent urban-scale to regional-scale (100 to 1,000 km) influences.

The annual satellite network consisted of 14 months of every-sixth-day, 24-hour sampling at 53 locations (including 35 PM_{2.5} sites, 20 PM_{2.5} organic compound sites [12 months of sampling between 02/06/00 and 01/31/01 only], and 7 PM₁₀ sites). The fall intensive study included daily 24-hour sampling of PM₁₀ between 10/09/00 and 11/14/00 at 11 sites. The winter intensive study included daily 24-hour sampling of PM_{2.5} on 13 forecast episode days at 25 sites. PM_{2.5} organic compound samples collected during the annual program were composited to one sample per site for gas chromatography/mass spectrometry analysis of particulate organics.

Table 1.1-2. below provides a summary of the filter analyses performed for the CRPAQS project.

Table 1.1-2

CRPAQS, AMBIENT DATA								
Anchor Sites	Sampling Sites	Sampling Period (dates)	Sampling Days (# days)	Sampling Interval (hours)	PM Size	EAF Analyses		
						Gravimetric Mass	XRF, IC, TOR ^j	AA, AC, Gases ^k
Winter Episodal ^{l,o} , SFS	Fresno, Angiola, (Bakersfield), Sierra Foothill, Bethel Island	12/15/00 to 02/03/01	15	3-13 hr	2.5	471	471	471
Annual, SFS	Fresno, Angiola, Bakersfield,	12/03/99 – 02/04/01	413	24hr	2.5	1229	290	
Summer Episodal Days, SFS ⁿ	Fresno	06/29/00 – 09/05/00	10	24hr	2.5	10	10	

Satellite Sites								
Sampling ^a	Sampling Sites for CMB	Sampling Period (dates)	Sampling Days (# days)	Sampling Interval (hours)	PM Size	EAF Analyses		
						Gravimetric Mass	XRF, IC, TOR ^j	AA, AC, Gases ^k
Annual (6 th Day) ^a	29 ^b	12/01/99 – 01/31/01	71 ^b	24hr	2.5	2329	1930	1930
Annual (6 th Day),	7 ^d	12/01/99 – 01/31/01	71 ^b	24hr	10	497	497	497
Annual (TIGF)	20 ^c	12/01/99 – 01/31/01	71 ^b composites	24hr	2.5			
Winter Episodal Days ⁱ	21 ^f	12/15/00 – 02/03/01	15 ⁱ	24hr	2.5	299	254	254
Fall Episodal Days	6 ^g	09/15/00 – 11/15/00	37	24hr	10	378	197	197

a. equipped with Minivol samplers

b. Every 6th day sampling based on US EPA compliance monitoring sites

c. 35 sites sampled, =29 for CMB: ACP*(72), BODG*(67), CLO*(66), COP*(71), FEDL*(38), FREM*(67), FRES*(67), HELM*(70), M14*(71), MRM*(72), PAC1(71), SELM*(71), SNFH*(70), SOH*(70), SWC*(70), VCS*(71), ALT1(68), BTI*(71), LVR1*(72), PLE*(70), S13*(69), SFA*(72), BRES*(45), CARP(63), CHL*(61), EDI(64), EDW*(50), FEL*(72), FELF*(70), KCW(64), MOP*(69), OLD*(66), OLW*(65), PIXL*(69), TEH2(65)

d. 7 sites sampled: COP, FSD, HAN, M14, VCS, BGS, OLD

e. 20 sites sampled, *= 14 for annual CMB composites: COP*, FEDL*, FRES*, FSF, HELM*, M14*, SJ4, SNFH*, YOSE1, BTI*, LVR1*, S13*, SDP, CHL*, EDW*, FEL*, OLW*, PIXL*, ANGI, BAC

f. 25 sites sampled, *=21 for CMB, (#sampling days): ACP* (13), ALT1 (10), BODG* (13), BRES* (13) CLO* (13), COP* (13), EDI (13), FEDL* (13), FEL* (13) FELF* (12), FREM* (12), FRES* (13), HELM* (13), KCW (13), LVR1* (13), M14* (13), MRM* (13), OLW* (12), PIXL* (13), S13* (12), SELM* (13), SOH* (13), SWC* (13), TEH2 (13), VCS* (13)

g. 11 sites sampled, *=6 for CMB, (#sampling days): SFE* (32), C05 (34) COP* (35), DAIP (35), DAIU (36), GRA* (37), GRAS* (28), H43* (32), HAN* (33), ORE (36), YOD (37)

h. 20 sites sampled on TIGF filters: 61, 24hr sampling days composite for each of 20 sites, 14 of these sites correspond to one of the 29 other satellite sites

i. Winter episodal days are 12/15,16,17,18,26,27,28/2000 and 1/4,5,6,7,31/2001 and 2/2,3/2001, 358 samples were for the IOP project while 113 additional samples were taken at Fresno only for the ETV study

j. XRF: Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Se, Br, Rb, Sr, Y, Zr, Mo, Au, Hg, Tl, Pb, U

AA: Na⁺, K⁺

IC: SO₄²⁻, NO₃⁻, Cl⁻

AC: NH₄⁺

TOR: O1TC, O2TC, O3TC, O4TC, E1TC, E2TC, E3TC

k. Gases: NH₃, HNO₃

2. FILTER MEASUREMENTS

The anchor sites annual sampling program used DRI medium-volume sequential filter samplers (SFS) equipped with Bendix 240 cyclone PM_{2.5} inlets and preceding anodized aluminum nitric acid denuders. Sampling was conducted daily, 24 hours/day (midnight to midnight) from 12/02/99 to 02/03/01 at a flow rate of 20 L/min. Two filter packs were used for sampling: 1) each Teflon/citric acid filter pack consists of a front Teflon-membrane filter (for mass, b_{abs} , and elemental analyses) backed up by a citric-acid-impregnated cellulose-fiber filter (for ammonia), and 2) each quartz/NaCl filter pack consists of a front quartz-fiber filter (for ion and carbon analyses) backed up by a sodium-chloride-impregnated cellulose-fiber filter (for volatilized nitrate).

Anchor site winter intensive sampling included both SFS for PM_{2.5} sampling and sequential gas samplers (SGS) for ammonia and nitric acid sampling by denuder difference on 15 forecast episode days (12/15/00 to 12/18/00, 12/26/00 to 12/28/00, 01/04/01 to 01/07/01, and 01/31/01 to 02/03/01). Sampling periods during the forecast days were 0000-0500, 0500-1000, 1000-1300, 1300-1600 and 1600-2400. The two SGS were equipped with: 1) citric-acid-coated glass denuders and quartz-fiber filters backed up by citric-acid-impregnated cellulose-fiber filters for ammonia (NH₃); and 2) anodized aluminum denuders and quartz-fiber filters backed up by sodium-chloride-impregnated cellulose-fiber filters for nitric acid (HNO₃).

The satellite annual sampling program used battery-powered Minivol samplers (Airmetrics, Eugene, OR) equipped with PM₁₀/PM_{2.5} (in tandem) or PM₁₀ inlets at a flow rate of 5 L/min.

Satellite site annual sampling program included every-sixth-day 24-hour sampling at 35 PM_{2.5} sites and 7 PM₁₀ sites between 12/02/99 and 02/03/01. Particulate organic compounds were sampled at 20 sites between 02/06/00 and 01/31/01.

Satellite site fall intensive study included 24-hour sampling of PM₁₀ on 37 days between 10/09/00 and 11/14/00 at 11 sites. 6 sites (COP, H43, HAN, GRA, GRAS, and SFE) were equipped with both Teflon/citric acid and quartz/NaCl filter packs. 5 sites (CO5, DAIP, DAIU, ORE, and YOD) were equipped with only Teflon/citric acid filter packs.

Satellite site winter intensive study included 24-hour sampling of PM_{2.5} on 13 forecast episode days (12/15/00 to 12/18/00, 12/25/00, 12/27/00, 12/28/00, 01/04/01 to 01/06/01, and 02/01/01 to 02/03/01) at 25 PM_{2.5} sites, with 21 of the sites equipped with both Teflon/citric acid and quartz/NaCl filter packs.

Minivol module A: PM_{2.5} Teflon/citric acid filter packs at 35 satellite sites. Each filter pack consisted of a front Teflon-membrane filter (for mass, b_{abs} , and elements) backed up by a citric-acid-impregnated cellulose-fiber filter (for ammonia).

Minivol module B: PM_{2.5} quartz/NaCl filter packs at 29 satellite sites (same sites as module A but excluding ALT1, PAC1, KCW, EDI, CARP, and TEH2). Each filter pack consisted of a front pre-fired quartz-fiber filter (for ions and carbon) backed up by a sodium-chloride-impregnated cellulose-fiber filter (for volatilized nitrate).

Minivol module D: PM_{2.5} Teflon-impregnated glass-fiber filters (TIGF) at a total of 20 sites (including 3 annual anchor sites [Fresno, Angiola, and Bakersfield], 14 annual satellite sites, the San Jose-4th St. [SJ4] site, the Sacramento-Del Paso Manor [SPP] site, and the Yosemite [YOSE1] site). A total of 61 samples acquired over the yearlong sampling period were composited as one sample and analyzed by gas chromatography with mass spectrometry (GC/MS) for 151 particulate organic compounds as listed in footnote d above.

Minivol module g: PM₁₀ Teflon/citric acid filter packs at 16 satellite sites, 4 of which (M14, VCS, COP, and OLD) were collocated with annual PM_{2.5} measurements, and 7 of which (M14, VCS, COP, FSD, BGS, HAN, and OLD) were annual PM₁₀ sites. Each filter pack consisted of a front Teflon-membrane filter (for mass, b_{abs}, and elements) backed up by a citric-acid-impregnated cellulose-fiber filter (for ammonia).

Minivol module h: PM₁₀ quartz/NaCl filter packs at 16 satellite sites, 4 of which were collocated with annual PM_{2.5} measurements (M14, VCS, COP, and OLD), and 7 of which (M14, VCS, COP, FSD, BGS, HAN, and OLD) were annual PM₁₀ sites. Each filter pack consisted of a front quartz-fiber filter (for ion and carbon analyses) backed up by a sodium-chloride-impregnated cellulose-fiber filter (for volatilized nitrate).

During the Anchor sites winter intensive the Fresno and Angiola sites were equipped with Micro Orifice Uniform Deposit Impactor (MOUDI) samplers. Three samplers were deployed at each site with one collecting Teflon substrates for mass and elemental analyses, a second collecting Teflon substrates for ion analyses and third collecting aluminum substrates for carbon analysis.

The MOUDI samplers were run on the winter intensive schedule's 15 forecast episode days but were run every other sampling period in order to allow for substrate changes between sampling periods. During the first winter sampling episode the MOUDIs were configured with the following stages, 5.62, 2.5, 1.8, 1.0, 0.56, 0.32, 0.18, 0.10 and <0.10 microns. After the first episode we obtained new 0.05 micron impaction plates from the manufacturer and shifted the cutpoints to 5.62, 2.5, 1.0, 0.56, 0.32, 0.18, 0.10, 0.05 and <0.05 microns for all subsequent samples.

2.1 Analysis Methods:

2.1.1 Gravimetric Analysis

Unexposed and exposed Teflon-membrane filters are equilibrated at a temperature of 21.5 ± 1.5 °C and a relative humidity of $35 \pm 5\%$ for a minimum of 24 hours prior to weighing. Weighing is performed on a Mettler MT-5 electro microbalance with ± 0.001 mg sensitivity. The charge on each filter is neutralized by exposure to a polonium source for 30 seconds before the filter is placed on the balance pan. The balance is calibrated with a 200 mg Class S weight and the tare is set prior to weighing each batch of filters. After every 10 filters are weighed, the calibration and tare are re-checked. If the results of these performance tests deviate from specifications by more than ± 5 mg, the balance is re-calibrated.

All initial filter weights are checked by an independent technician. Samples are re-weighed if these check-weights do not agree with the original weights within ± 0.010 mg. At least 30% of the exposed filter weights are checked by an independent technician. Samples are re-weighed if these check-weights do not agree with the original weights within ± 0.015 mg. Pre- and post-weights, check weights, and re-weights (if required) are recorded on data sheets and are directly entered into a data base via an RS232 connection. All weights are entered by filter number into the DRI aerosol data base.

2.1.2 Elements by XRF

After gravimetric analysis, samples collected on the Teflon-membrane filters were analyzed by energy dispersive X-ray fluorescence (ED-XRF, Kevex 0700) for the following 40 elements: sodium (Na), magnesium (Mg), aluminum (Al), silicon (Si), phosphorus (P), sulfur (S), chlorine (Cl), potassium (K), calcium (Ca), titanium (Ti), vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), gallium (Ga), arsenic (As), selenium (Se), bromine (Br), rubidium (Rb), strontium (Sr), yttrium (Y), zirconium (Zr), molybdenum (Mo), palladium (Pd), silver (Ag), cadmium (Cd), indium (In), tin (Sn), antimony (Sb), barium (Ba), gold (Au), mercury (Hg), thallium (Tl), lead (Pb), lanthanum (La), and uranium (U).

Calibration is performed using thin film standards from Micromatter Inc. A multielement thin film standard is analyzed with each run to monitor for calibration drift and is used as the indicator for routine calibrations.

2.1.3 Elemental and Organic Carbon

The thermal/optical reflectance (TOR) method measures organic (OC) and elemental (EC) carbon. The TOR method is based on the principle that different types of carbon-containing particles are converted to gases under different temperature and oxidation conditions. The different carbon fractions from TOR are useful for comparison with

other methods which are specific to a single definition for OC and EC. These specific carbon fractions also help distinguish among seven carbon fractions reported by TOR:

- The carbon evolved in a helium atmosphere at temperatures between ambient and 120 °C (OC1)
- The carbon evolved in a helium atmosphere at temperatures between 120 °C and 250 °C (OC2)
- The carbon evolved in a helium atmosphere at temperatures between 250 °C and 450 °C (OC3)
- The carbon evolved in a helium atmosphere between 450 °C and 550 °C (OC4)
- The carbon evolved in an oxidizing atmosphere at 550 °C (EC1)
- The carbon evolved in an oxidizing atmosphere between 550 °C and 700 °C (EC2)
- The carbon evolved in an oxidizing atmosphere between 700 °C and 800 °C (EC3)

The thermal/optical reflectance carbon analyzer consists of a thermal system and an optical system. The thermal system consists of a quartz tube placed inside a coiled heater. Current through the heater is controlled to attain and maintain pre-set temperatures for given time periods. A portion of a quartz filter is placed in the heating zone and heated to different temperatures under non-oxidizing and oxidizing atmospheres. The optical system consists of a He-Ne laser, a fiber optic transmitter and receiver, and a photocell. The filter deposit faces a quartz light tube so that the intensity of the reflected laser beam can be monitored throughout the analysis.

As the temperature increases from ambient (~25 °C) to 550 °C, organic carbon compounds are volatilized from the filter in a non-oxidizing (He) atmosphere while elemental carbon is not oxidized. When oxygen is added to the helium at temperatures greater than 550 °C, the elemental carbon burns and enters the sample stream. The evolved gases pass through an oxidizing bed of heated manganese dioxide where they are oxidized to carbon dioxide, then across a heated nickel catalyst which reduces the carbon dioxide to methane (CH₄). The methane is then quantified with a flame ionization detector (FID).

The reflected laser light is continuously monitored throughout the analysis cycle. The negative change in reflectance is proportional to the degree of pyrolytic conversion from

organic to elemental carbon which takes place during organic carbon analysis. After oxygen is introduced, the reflectance increases rapidly as the light-absorbing carbon is burned off the filter. The carbon measured after the reflectance attains the value it had at the beginning of the analysis cycle is classified as elemental carbon. This adjustment for pyrolysis in the analysis is significant, as high as 25% of organic or elemental carbon, and it cannot be ignored.

The system is calibrated by analyzing samples of known amounts of methane, carbon dioxide, and potassium hydrogen phthalate (KHP). The FID response is ratioed to a reference level of methane injected at the end of each sample analysis. Performance tests of the instrument calibration are conducted at the beginning and end of each day's operation. Intervening samples are re-analyzed when calibration changes of more than $\pm 10\%$ are found.

Known amounts of American Chemical Society (ACS) certified reagent grade crystal sucrose and KHP are committed to TOR as a verification of the organic carbon fractions. Fifteen different standards are used for each calibration. Widely accepted primary standards for elemental and/or organic carbon are still lacking. Results of the TOR analysis of each filter are entered into the DRI data base.

2.1.4 Inorganic Ion Analyses

Water-soluble chloride, nitrate, sulfate, ammonium, sodium, and potassium are obtained by extracting the quartz-fiber particle filter in 15 ml of deionized-distilled water (DDW). The extraction vials are capped and sonicated for 60 minutes, shaken for 60 minutes, then aged overnight to assure complete extraction of the deposited material in the solvent. The ultrasonic bath water is monitored to prevent temperature increases from the dissipation of ultrasonic energy in the water. After extraction, these solutions are stored under refrigeration prior to analysis.

2.1.5 Ion Chromatographic Analysis for Chloride, Nitrate, and Sulfate

Water-soluble chloride (Cl^-), nitrate (NO_3^-), and sulfate (SO_4^{2-}) are measured with the Dionex 2020i (Sunnyvale, CA) ion chromatograph (IC). In IC, an ion-exchange column separates the sample ions in time for individual quantification by a conductivity detector. Prior to detection, the column effluent enters a suppressor column where the chemical composition of the component is altered, resulting in a matrix of low conductivity. The ions are identified by their elution/retention times and are quantified by the conductivity peak area. Approximately 2 ml of the filter extract are injected into the ion chromatograph. The resulting peaks are integrated and the peak integrals are converted to concentrations using calibration curves derived from solution standards. The Dionex system for the analysis of Cl^- , NO_3^- , and SO_4^{2-} contains a guard column (AG4a column, Cat. No. #37042), an anion separator column (AS4a column, Cat. No. #37041) with a strong basic anion exchange resin, and an anion micro membrane suppressor column (250 \times 6 mm ID) with a strong acid ion exchange resin. The anion eluent consists of

sodium carbonate (Na_2CO_3) and sodium bicarbonate (NaHCO_3) prepared in DDW. The DDW is verified to have a conductivity of less than 1.8×10^{-5} ohm/cm prior to preparation of the eluent. For quantitative determinations, the ion chromatograph is operated at a flow rate of 2.0 ml/min.

The primary standard solution containing NaCl, NaNO_3 , and $(\text{Na})_2\text{SO}_4$ is prepared with reagent grade salts dried in an oven at 105 °C for one hour and then brought to room temperature in a desiccator. These anhydrous salts are weighed to the nearest 0.10 mg on a routinely calibrated analytical balance under controlled temperature (~ 20 °C) and relative humidity ($\pm 30\%$) conditions. These salts are diluted in precise volumes of DDW. Calibration standards are prepared at least once each month by diluting the primary standard solution to concentrations covering the range expected in the filter extracts. These standards are then stored in a refrigerator. The calibration concentrations prepared are at 0.1, 0.2, 0.5, 1.0, and 2.0 mg/ml for each of the analysis species.

Calibration curves are performed weekly. Chemical compounds are identified by matching the retention time of each peak in the unknown sample with the retention times of peaks in the chromatograms of the standards. A DDW blank is analyzed after every 20 samples and a calibration standard is analyzed after every 10 samples. These quality control checks verify the baseline and the calibration, respectively. Environmental Research Associates (ERA, Arvada, CO) standards are used daily as an independent quality assurance (QA) check. These standards (ERA Wastewater Nutrient and ERA Mineral WW) are traceable to NIST simulated rainwater standards. If the values obtained for these standards do not coincide within a pre-specified uncertainty level (typically three standard deviations of the baseline level or $\pm 5\%$), the samples between that standard and the previous calibration standards are re-analyzed.

After analysis, the printout for each sample in the batch is reviewed for the following: 1) proper operational settings, 2) correct peak shapes and integration windows, 3) peak overlaps, 4) correct background subtraction, and 5) quality control sample comparisons. When values for replicates differ by more than $\pm 10\%$ or values for standards differ by more than $\pm 5\%$, samples before and after these quality control checks are designated for re-analysis in a subsequent batch. Individual samples with unusual peak shapes, background subtractions, or deviations from standard operating parameters are also designated for re-analysis.

Using the same IC analysis procedure, water soluble nitrate and nitric acid concentrations are obtained from the NaCl impregnated cellulose backup filter and the denuded and non-denuded filter packs from the Nitric Acid Sequential Gas Samplers (SGS).

2.1.6 Ammonium Analysis

An Astoria 2 AC system (Astoria-Pacific, Clackamas, OR) was used to measure NH_4^+ concentration by the indolphenol method. Each sample was mixed with reagents and subjected to appropriate reaction periods before submission to the colorimeter. Beer's

Law relates the liquid's absorbency to the amount of the ion in the sample. A photomultiplier tube measured this absorbency through an interference filter, which is specific to NH_4^+ . Two ml of extract in a sample vial were placed in a computer-controlled autosampler. Calibration curves are produced with each daily batch of samples.

The same analysis method was used for the determination of ammonia concentrations from the citric acid impregnated backup filters as well as the denuded and non-denuded filter packs from the Ammonia Sequential Gas Samplers (SGS).

2.1.7 Atomic Absorption Analysis for Soluble metals

Soluble sodium, magnesium, potassium and calcium were measured using a Varian Spectra AA-880 atomic absorption spectrophotometer. In atomic absorption spectrophotometry the sample is aspirated into a flame and atomized. A light beam from a hollow cathode lamp is directed through the flame, into a monochromator, and onto a photoelectric detector that measures the amount of light absorbed by the atomized element in the flame. The cathode of a hollow cathode lamp contains the pure metal which results in a line source emission spectrum. Since each element has its own characteristic absorption wavelength, the source lamp composed of that element is used. The amount of energy of the characteristic wavelength absorbed in the flame is proportional to the concentration of the element in the sample. Calibration curves are produced with each daily batch of samples.

Table 2.1-1. Minimum detectable limits (MDLs) of chemical species using DRI standard analysis protocols.

<u>Species</u>	<u>Analysis Method^a</u>	<u>MDL^b ($\mu\text{g}/\text{filter}$)</u>	<u>MDL^c ($\mu\text{g}/\text{m}^3$)</u>
Chloride (Cl^-)	IC	1.5005	0.0625
Nitrite (NO_2^-)	IC	1.5005	0.0625
Nonvolatilized Nitrate (NO_3^-)	IC	1.5005	0.0625
Volatilized Nitrate (NO_3^-)	IC	1.5005	0.0625
Nitric Acid (HNO_3)	IC	1.5005	0.0625
Sulfate ($\text{SO}_4^{=}$)	IC	1.5005	0.0625
Ammonium (NH_4^+)	AC	1.5005	0.0625
Ammonia (NH_3)	AC	1.5005	0.0625
Soluble Sodium (Na^+)	AAS	0.2362	0.0098
Soluble Magnesium (Mg^{++})	AAS	0.0547	0.0023
Soluble Potassium (K^+)	AAS	0.1498	0.0062
Soluble Calcium (Ca^{++})	AAS	0.0979	0.0041
Organic Carbon (OC)	TOR	2.7590	0.1150
Elemental Carbon (EC)	TOR	2.7590	0.1150
Sodium (Na)	XRF	0.9533	0.0397
Magnesium (Mg)	XRF	0.3456	0.0144
Aluminum (Al)	XRF	0.1382	0.0058
Silicon (Si)	XRF	0.0864	0.0036
Phosphorus (P)	XRF	0.0778	0.0032
Sulfur (S)	XRF	0.0691	0.0029
Chlorine (Cl)	XRF	0.1382	0.0058
Potassium (K)	XRF	0.0835	0.0035
Calcium (Ca)	XRF	0.0634	0.0026
Titanium (Ti)	XRF	0.0403	0.0017
Vanadium (V)	XRF	0.0346	0.0014
Chromium (Cr)	XRF	0.0259	0.0011
Manganese (Mn)	XRF	0.0230	0.0010
Iron (Fe)	XRF	0.0202	0.0008
Cobalt (Co)	XRF	0.0115	0.0005
Nickel (Ni)	XRF	0.0115	0.0005
Copper (Cu)	XRF	0.0144	0.0006
Zinc (Zn)	XRF	0.0144	0.0006
Gallium (Ga)	XRF	0.0259	0.0011

Table 2.1-1. (continued)

<u>Species</u>	<u>Analysis Method^a</u>	<u>MDL^b ($\mu\text{g}/\text{filter}$)</u>	<u>MDL^c ($\mu\text{g}/\text{m}^3$)</u>
Arsenic (As)	XRF	0.0230	0.0010
Selenium (Se)	XRF	0.0173	0.0007
Bromine (Br)	XRF	0.0144	0.0006
Rubidium (Rb)	XRF	0.0144	0.0006
Strontium (Sr)	XRF	0.0144	0.0006
Yttrium (Y)	XRF	0.0173	0.0007
Zirconium (Zr)	XRF	0.0230	0.0010
Molybdenum (Mo)	XRF	0.0374	0.0016
Palladium (Pd)	XRF	0.1526	0.0064
Silver (Ag)	XRF	0.1670	0.0070
Cadmium (Cd)	XRF	0.1670	0.0070
Indium (In)	XRF	0.1786	0.0074
Tin (Sn)	XRF	0.2333	0.0097
Antimony (Sb)	XRF	0.2477	0.0103
Barium (Ba)	XRF	0.7171	0.0299
Lanthanum (La)	XRF	0.8554	0.0356
Gold (Au)	XRF	0.0432	0.0018
Mercury (Hg)	XRF	0.0346	0.0014
Thallium (Tl)	XRF	0.0346	0.0014
Lead (Pb)	XRF	0.0403	0.0017
Uranium (U)	XRF	0.0317	0.0013

^a IC = ion chromatography. AC = automated colorimetry. AAS = atomic absorption spectrophotometry. TOR = thermal/optical reflectance. XRF = x-ray fluorescence.

^b Minimum detectable limit (MDL) is the concentration at which instrument response equals three times the standard deviation of the response to a known concentration of zero.

^c MDL assuming a nominal sample volume of 24 cubic meters

2.2 Measurement Validity

All of the filtered-based measurements are validated. Ninety-five percent of the samples passed the Level I and Level II tests.

Level II data validation was performed as each batch of analysis data was completed. Individual database files are saved in spreadsheet programs to allow linear regression plotting of the following: sum of measured species versus mass, sulfate versus total sulfur, chloride versus total chlorine, soluble potassium versus total potassium, measured anions versus measured cations, and measured versus predicted ammonium.

Mass and elemental measurements done on the Teflon filters are non-destructive thus allowing reanalysis if needed. Quartz and cellulose filters are quantitatively cut in half, with one half being extracted and analyzed and the second half archived for future

analysis if needed.

Plot outliers were identified and these filter pairs were further scrutinized by rechecking field data and analysis results and applying flags as appropriate. If no problems were identified with the field data or the original analysis results the filter was sent for reanalysis. Reanalysis results were merged into the database and a replicate 'r', flag was added to that analysis method flag field. Analysis data not flagged as void, 'v', are considered to be valid when the validation flags (field and analysis) are included with the data point.

The measured sum of species should be less than or equal to the gravimetrically determined mass concentration. Figure 2.2-1 below is the plot of the PM₁₀ satellite sites data that shows good agreement overall with four obvious plot outliers above the regression line, these filter pairs were reanalyzed and flagged. Similar plots for all of the CRPAQS data have been produced.

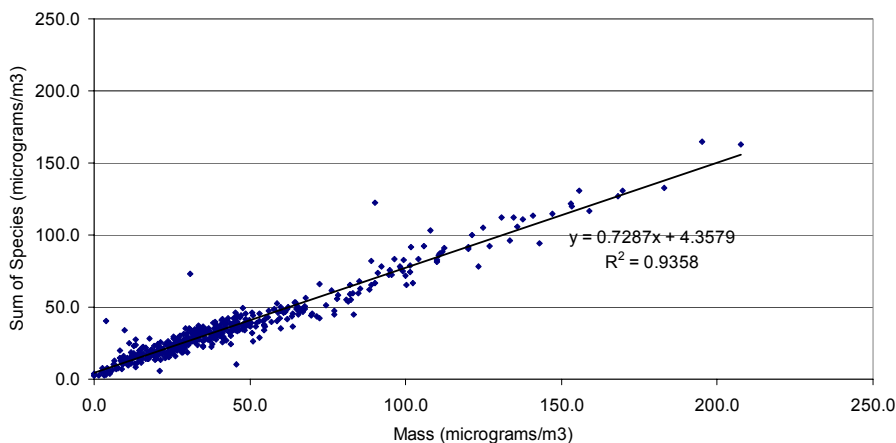


Figure 2.2-1. Summed PM₁₀ mass versus gravimetric PM₁₀ mass during CRPAQS.

The validation plot for measured versus calculated ammonium for the PM₁₀ satellite sites is shown in Figure 2.2-2 below, good agreement is shown for the independent measurements (measured by automated colorimetry and calculated by ion chromatography) of particulate ammonium thereby validating the data from both methods.

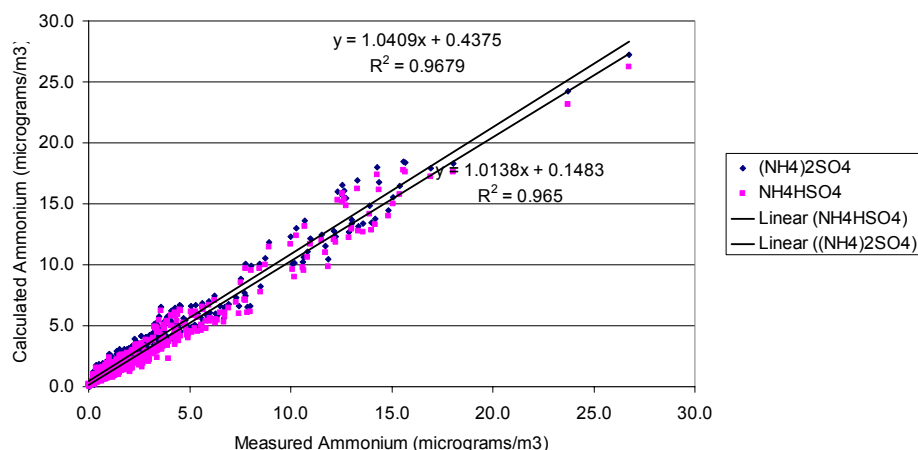


Figure 2.2-2. Comparisons between measured ammonium and calculated ammonium based on nitrate and sulfate measurements.

The ratio of measured anions to measured cations showed very good agreement in the CRPAQS datasets, for example, the PM₁₀ satellite sites data has a slope of 1.07 with a correlation coefficient of 0.98, this shows that adequate ions for closure in the ion balance were measured during the study.

Validation of all of the physical consistency of the measurement data is done in an analogous manner, with each of the checks listed above performed for each dataset.

3.DATABASE STRUCTURES AND FEATURES

The raw CRPAQS data was processed with Microsoft FoxPro 2.6 for Windows (Microsoft Corp., 1994), a commercially available relational database management system. FoxPro can handle 256 fields of up to 4,000 characters per record and up to one billion records per file. The data base files (*.DBF) can also be read directly into a variety of popular statistical, plotting, data base, and spreadsheet programs without requiring any specific conversion software. After processing, the final CRPAQS data were converted from FoxPro to Microsoft Excel format for reporting purposes.

In FoxPro, one of five field types (character, date, numerical, logical, or memo) was assigned to each observable. Sampling sites and particle size fractions are defined as “character” fields, sampling dates are defined as “date” fields, and measured data are defined as “numeric” fields. “logical” fields are used to represent a “yes” or “no” value applied to a variable, and “memo” fields accommodate large blocks of text and are used to document the data validation results.

Data contained in different XBase files can be linked by indexing on and relating to common attributes in each file. Sampling site, sampling hour, sampling period, particle size, and sampling substrate IDs are, typically, the common fields that can be used to relate data in one file to the corresponding data in another file.

To assemble the final data files, information was merged from many data files derived from field monitoring and laboratory analyses by relating information on the common fields cited above.

Measurement precisions were propagated from precisions of the volumetric measurements, the chemical composition measurements, and the field blank variability using the methods of Bevington (1969) and Watson et al. (1995). The following equations calculated the precision associated with filter-based measurements:

$$C_i = (M_i - B_i)/V \quad (3-1)$$

$$V = F \times t \quad (3-2)$$

$$B_i = \frac{1}{n} \sum_{j=1}^n B_{ij} \text{ for } B_i > \sigma_{Bi} \quad (3-3)$$

$$B_i = 0 \text{ for } B_i \leq \sigma_{Bi} \quad (3-4)$$

$$\sigma_{Bi} = \text{STD}_{Bi} = \left[\frac{1}{n-1} \sum_{j=1}^n (B_{ij} - B_i)^2 \right]^{1/2} \text{ for } \text{STD}_{Bi} > \text{SIG}_{Bi} \quad (3-5)$$

$$\sigma_{Bi} = \text{SIG}_{Bi} = \left[\frac{1}{n} \sum_{j=1}^n (\sigma_{Bij})^2 \right]^{1/2} \text{ for } \text{STD}_{Bi} \leq \text{SIG}_{4Bi} \quad (3-6)$$

$$\sigma_{Ci} = \left[\frac{\sigma_{Mi}^2 + \sigma_{Bi}^2}{V^2} + \frac{\sigma_v^2 (M_i - B_i)^2}{V^4} \right]^{1/2} \quad (3-7)$$

$$\sigma_{\text{RMS}_i} = \left(\frac{1}{n} \sum_{j=1}^n \sigma_{\text{Ci}}^2 \right)^{1/2} \quad (3-8)$$

$$\sigma_V/V = 0.05 \quad (3-9)$$

where:

B_i	=	average amount of species i on field blanks
B_{ij}	=	the amount of species i found on field blank j
C_i	=	the ambient concentration of species i
F	=	flow rate throughout sampling period
M_i	=	amount of species i on the substrate
M_{ijf}	=	amount of species i on sample j from original analysis
M_{ijr}	=	amount of species i on sample j from replicate analysis
n	=	total number of samples in the sum
SIG_{Bi}	=	the root mean square error (RMSE), the square root of the averaged sum of the squared of σ_{Bij} .
STD_{Bi}	=	standard deviation of the blank
σ_{Bi}	=	blank precision for species i
σ_{Bij}	=	precision of the species i found on field blank j
σ_{Ci}	=	propagated precision for the concentration of species i
σ_{Mi}	=	precision of amount of species i on the substrate
σ_{RMS_i}	=	root mean square precision for species i
σ_V	=	precision of sample volume
t	=	sample duration
V	=	volume of air sampled

Dynamic field blanks were periodically placed in each sampling system without air being drawn through them to estimate the magnitude of passive deposition for the period of time which filter packs remained in a sampler. No statistically significant inter-site differences in field blank concentrations were found for any species after removal of outliers (i.e., concentration exceeding three times the standard deviations of the field blanks). The average field blank concentrations (with outliers removed) were calculated for each species on each substrate (e.g., Teflon-membrane, quartz-fiber), irrespective of the sites.

Blank precisions (σ_{Bi}) are defined as the higher value of the standard deviation of the blank measurements, STD_{Bi} , or the square root of the averaged squared uncertainties of the blank concentrations, SIG_{Bi} . If the average blank for a species was less than its precision, the blank was set to zero (as shown in Equation 3-4). The precisions (σ_{Mi}) for XRF analysis were determined from counting statistics unique to each sample. Hence, the σ_{Mi} is a function of the energy-specific peak area, the background, and the area under the baseline.

4. REFERENCES

- Watson, J.G.; Chow, J.C.; and Frazier, C.A. (1999). X-ray fluorescence analysis of ambient air samples. In *Elemental Analysis of Airborne Particles, Vol. 1*, S. Landsberger and M. Creatchman, Eds. Gordon and Breach Science, Amsterdam, pp. 67-96.
- Chow, J.C.; and Watson, J.G. (1999). Ion chromatography in elemental analysis. In *Elemental Analysis of Airborne Particles, Vol. 1*, S. Landsberger and M. Creatchman, Eds. Gordon and Breach Science, Amsterdam, pp. 97-137.
- Bevington, P.R. (1969). *Data Reduction and Error Analysis for the Physical Sciences*. McGraw Hill, New York, NY.
- Watson, J.G.; Liroy, P.J.; and Mueller, P.K., (1995). The measurement process: Precision, accuracy, and validity. In *Air Sampling Instruments for Evaluation of Atmospheric Contaminants*, Cohen, B.S. and Hering, S.V., editors. American Conference of Governmental Industrial Hygienists, Cincinnati, OH, pp. 187-194.